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ACIDIFIED CATCHMENT OF CENTRAL ONTARIO

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ABSTRACT

In Plastic Lake catchment, Ontario, Canada, there are two patterns of trace metal transport. One pattern (Pb, Cu) can be explained by the metals' affinity for dissolved organic carbon (DOC). The other pattern (Cd, Zn) can be explained by the metals' solubility in dilute acid and mineral soils. These two patterns are observed when following in sequence the aqueous metal concentrations (i) first in the precipitation and then through the catchment to (ii) a low DOC, acidified, upland soil water seep, (iii) a high DOC wetland outflow and (iv) Plastic Lake outflow. Despite the highest relative values of Pb and Cu in precipitation, they have their lowest median concentrations at the soil water seep, elevated concentrations at the wetland outflow and then lower concentrations at the lake outflow. The pattern is identical to that of DOC and organic Al. Clearly the high DOC at (iii) dominates transport through the catchment, while the low DOC at (ii) reduces transport from the upland soils. In contrast, the other metals (Cd, Zn) exhibit their highest median concentrations at the acidified soil water seep (ii) and reduced values further downstream. With this group, soil acidification rather than DOC appears to be the major factor enhancing metal transport.

INTRODUCTION

The anthropogenic acidity of atmospheric deposition has caused increased export of Al, Mn and possibly trace metals from acidified catchments (for reviews see Campbell et al., 1985; LaZerte, 1986). The objective of this study was to document the deposition of trace metals onto a small acidified catchment in the Muskoka–Haliburton region of Central Ontario, and to determine from where and to where in the catchment they were being transported, if at all.

EXPERIMENTAL

Sampling methods

Trace metals in precipitation were sampled by installing commercially manufactured, nylon-reinforced polyethylene bags into Teflon coated wet-only collectors. The bags were not pre-cleaned in any way, but each lot from the manufacturer was tested for contamination before being put into use. The wet-only collectors were inspected weekly and if sufficient sample was available, the bag was replaced. Bags were allowed to remain in the collector for a maximum of 1 month. They were transported within an outer bag, and installed and removed with talc-free polyethylene gloves. In a Class 100 clean room, the bags were acidified to 0.1% with Seastar quartz distilled nitric acid. The double bags were stored in the clean room until analysis.

Monthly field quality control samples (QCP) consisted of new bags taken to a wet-only collector, installed, the lid closed then opened, removed and then returned to the clean room. One litre of DDW (double deionized water) was then added to the bag and acidified as usual.

Trace metals in surface waters were sampled weekly with pre-cleaned, 500 ml Teflon or linear polyethylene bottles stored in polyethylene bags. The bottle pre-cleaning procedure is outlined in Table 1. The bagged bottles were transported in an outer bag, and the samples were collected while wearing talc-free polyethylene gloves. In a Class 100 clean room, the bottles were acidified to 0.1% with Seastar quartz distilled nitric acid. The bagged bottles were stored in the clean room until analysis.

Weekly field quality control samples (QC) consisted of pre-cleaned bottles that were filled with DDW in the clean room, bagged, taken to the sample sites, opened for 3 min, closed and returned to the clean room for acidification as usual.

1

Analytical methods

Cadmium was analyzed by graphite furnace atomic absorption spectroscopy (GFAAS) with automated sample injection. Zinc and Cu were measured using a Metrohm hanging mercury drop anodic stripping voltammeter (DPASV). Lead was also measured by DPASV, but with an E.G. and G. Rotel rotating glassy carbon electrode. All DPASV calibrations were by standard addition, but a calibration curve was calculated for each Cd run on the GFAAS. There was no other sample modification, filtration, pre-concentration or digestion other than the initial 0.1% nitric acid addition.

The detection limits for these methods have been determined to be 0.01, 0.03,

TABLE 1

Bottle cleaning procedure for trace metal collection

— Rinse with SDW[a]; soak in Acationex bath for 2h
— Shake with Acationex for 2 min; rinse with DDW[b]
— Shake with chromic[c] acid for 2 min; rinse with DDW

The following is performed in a Class 100 clean room:

— Fill with 2.5% nitric acid[d]; soak for 48 h in 5% nitric acid[d]
— Rinse six times with DDW and store in polyethylene bags

[a] SDW is single deionized water after reverse osmosis.
[b] DDW is SDW passed through a Barnstead UltraPure deionizer.
[c] Chromic acid is made by dissolving 25 ml of chromium trioxide in 4 l of sulphuric acid.
[d] Percentage by volume of Baker Instra Analyzed concentrated nitric acid.

0.3 and $0.5 \mu g l^{-1}$ for Cd, Pb, Cu and Zn, respectively (unpublished results, Laboratory Services Branch, Ontario Ministry of the Environment, Dorset Ont., 1988). Temporary problems with the E.G. and G. Rotel rotating carbon electrode system reduced the number of Pb samples analyzed during this investigation relative to the others.

Sampling locations and duration

Trace metals in precipitation were collected at three sites located within 50 km of Dorset, Ontario: Plastic Lake (PCP2), Paint Lake (PT1P) and Harp Lake (HPP2) catchments. The period of record for these collectors extends from April 1987 to May 1988 for PT1P (the longest), and from January 1988 to April 1988 for HPP2 (the shortest).

Besides the precipitation collector, surface water samples were also collected at three locations in Plastic Lake catchment. These sites were chosen to represent a typical flow path of water through the catchment (Fig. 1). PC1-08 represents water that has only passed through the forest canopy and upland soils. There is little wetland upstream of this site. PC1 is downstream of PC1-08 and represents water that has subsequently passed through a perennially wet, organic-rich, highly reducing minerotrophic conifer/spagnum swamp. Downstream of these two sites is PCO, the outflow of Plastic Lake. This site demonstrates the impact of within-lake processes on water chemistry. Additional information on these and other sites in the Plastic Lake catchment
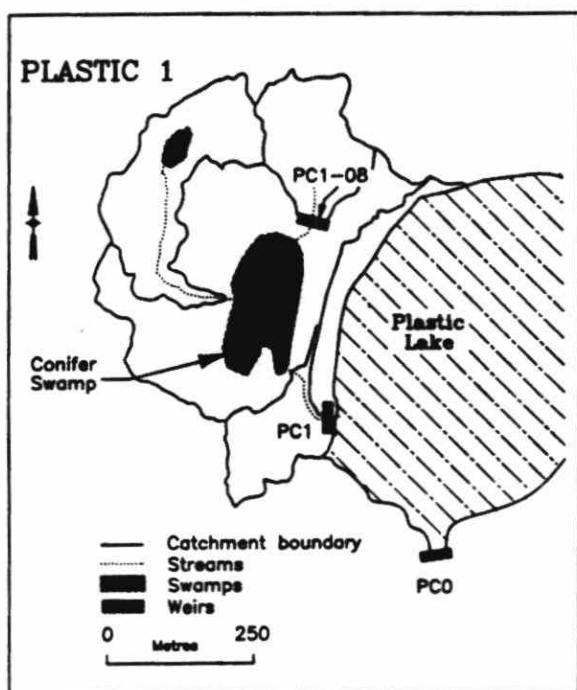

Fig. 1. Plastic Lake and the surface water sampling locations.

can be obtained from LaZerte (1984, 1989), LaZerte and Dillon (1984, 1985), Dillon et al. (1987) and France and LaZerte (1987).

The surface water samples were collected between April 1987 and May 1988. As PC1-08 stops flowing in the summer, the frequency of sample collection was lower than the other sites. Because of its erratic chemistry (LaZerte and Dillon, 1985), PC1 was sampled more frequently than PCO.

3

Data manipulation

The extreme asymmetry and non-normality of the data collected, and the frequent presence of outliers (most of which appeared to be real) dictated a non-parametric approach to the data presentation and analysis. Medians, as well as upper and lower quartiles (between which 50% of the data falls), are presented in Tables 1 and 2, along with the sample size. To expedite the comparison of stations, the data are also presented using notched box plots (e.g., Fig. 2). The left and right ends of each box represent the lower and upper quartiles, respectively, while the central vertical line gives the median. The end of the right "whisker" is the largest datum which falls within the upper quartile plus 1.5 times the inter-quartile range. The end of the left "whisker"

TABLE 2

Precipitation metal concentrations ($\mu g \, l^{-1}$); lower quartile, median, upper quartile, and n at four stations (see text for definitions)

Site	Cd	Pb	Cu	Zn
QCP				
	< 0.01	< 0.03	< 0.3	< 0.5
Median	< 0.01	< 0.03	< 0.3	< 0.5
	< 0.01	< 0.03	< 0.3	< 0.5
n	7	7	9	9
HPP2				
	0.08	1.00	0.9	3.4
Median	0.11	3.09	1.2	4.0
	0.20	5.42	1.5	6.4
n	15	13	15	15
PCP2				
	0.03	1.34	0.7	2.7
Median	0.10	1.86	1.1	3.7
	0.26	3.71	1.6	5.5
n	44	27	41	40
PT1P				
	0.01	1.25	0.7	1.4
Median	0.05	2.17	1.0	3.7
	0.18	4.81	1.6	6.3
n	63	44	61	60

is the smallest datum which falls within the lower quartile minus 1.5 times the inter-quartile range. Values outside the whiskers are indicated as (∗) or (O), depending upon how far out they are. The width of the "notch" gives an approximate 95% confidence interval about the median which can be used to evaluate differences between a pair of stations or between a station and the field quality controls (Chambers et al., 1983). In order to compare the "notches" visually, it was often necessary to increase the width of the boxes by excluding some of the largest outside values from the plot. All statistics and statistical graphics were obtained from the computer programs SYSTAT and SYGRAPH.

RESULTS

Despite initial concerns about using uncleaned, commercial bags for our wet-only precipitation collection, the rain in the Muskoka–Haliburton area was sufficiently polluted with metals (Table 2 and Fig. 2) to far exceed values in our monthly field quality control samples (QCP). As there was no apparent difference between the collectors, all data were combined to provide a total precipitation value (PRECIP) for subsequent comparisons. The medians of this overall precipitation data set are 0.08, 2.28, 1.1 and $3.7 \mu g \, l^{-1}$ for Cd, Pb, Cu and Zn, respectively.

TABLE 3

Surface water metal concentrations ($\mu g \, l^{-1}$), pH and DOC ($mg \, l^{-1}$); lower quartile, median, upper quartile, and n at four stations (see text for definitions)

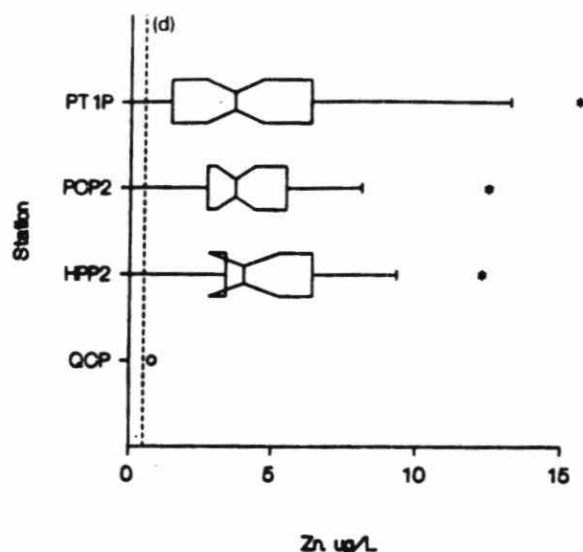| Site	Cd	Pb	Cu	Zn	pH	DOC
QC						
	< 0.01	< 0.03	< 0.5			
Median	< 0.01	< 0.03	< 0.3	< 0.5		
	0.02	< 0.03	0.4	< 0.5		
n	92	60	95	95		
PC1-08						
	0.09	0.06	< 0.3	18.6	4.87	1.5
Median	0.15	0.08	0.3	22.6	4.93	1.8
	0.17	0.14	0.5	25.9	5.01	1.9
n	42	42	42	42	80	79
PC1						
	0.08	0.34	0.5	9.9	4.37	8.8
Median	0.14	0.64	0.7	18.1	4.48	10.9
	0.27	0.94	1.2	28.3	4.63	13.9
n	71	71	73	73	85	84
PC0						
	< 0.01	0.17	< 0.3	1.1	5.55	1.8
Median	0.01	0.20	0.5	2.9	5.67	2.1
	0.05	0.30	0.8	4.6	5.75	2.3
n	53	37	53	53	98	97

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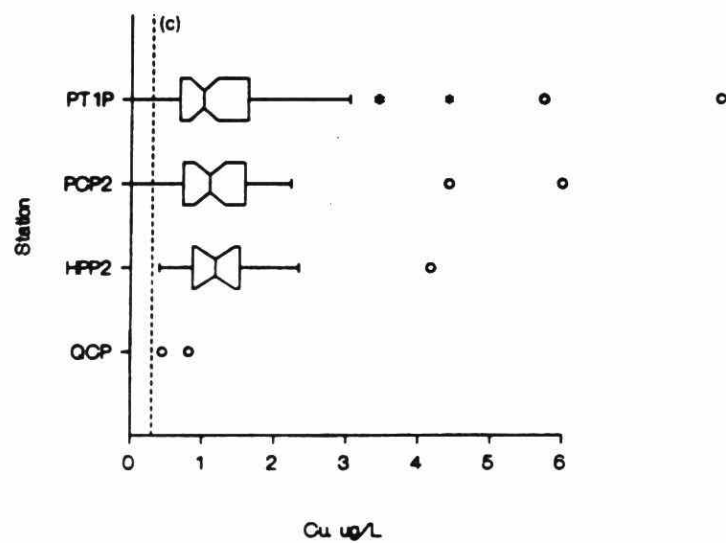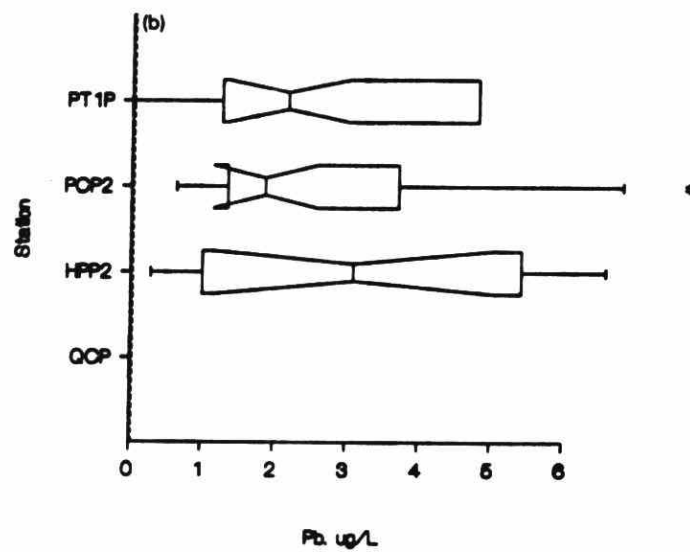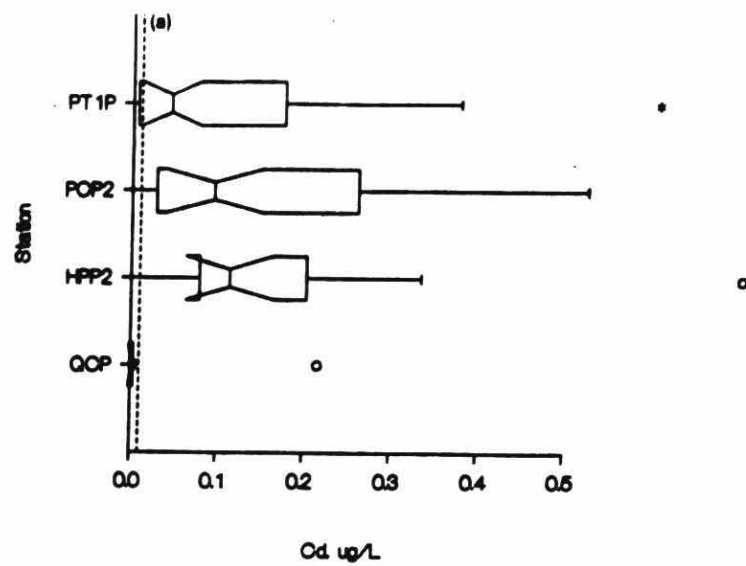
Fig. 2. Notched box plots of Cd, Pb, Cu and Zn from the three wet-only precipitation collectors and the precipitation field quality control samples (QCP).

PRECIP and QCP are compared with the surface water samples and their field quality controls (QC) in Fig. 3 (see also Table 3). Except for one case, the QCs are all significantly lower than values for the surface water stations. Copper and Cd have the most severe problems with respect to detection limits. The confidence interval for Cd at PCO overlaps the detection limit $(0.01 \, \mu g \, l^{-1})$ and is not significantly different from the field QCs. Similarly for Cu at PC1-08, the confidence interval overlaps the detection limits $(0.3 \, \mu g \, l^{-1})$.

In the case of the QCs for Cu and Cd, there are several outside values which are probably the result of an erratically malfunctioning deionizer unit providing poor quality field blank water. The deionizer malfunction appeared to have little impact on regular samples, perhaps because bottles were thoroughly rinsed three times with sample before field collection.

The metals can be split into two groups according to how their relative concentrations change through the ecosystem. The Pb–Cu group exhibits its highest median concentrations in precipitation and its lowest median concentrations immediately "downstream" at PC1-08, the upland soil water seep. Concentrations then become elevated again in the wetland outflow (PC1) and finally decline in the lake (PC0).

Conversely, the Cd–Zn group exhibits its highest concentrations at PC1-08. These concentrations tend to decline in the wetland (PC1), but then dramatically decline in the lake (PC0). PRECIP concentrations of Cd and Zn are intermediate.
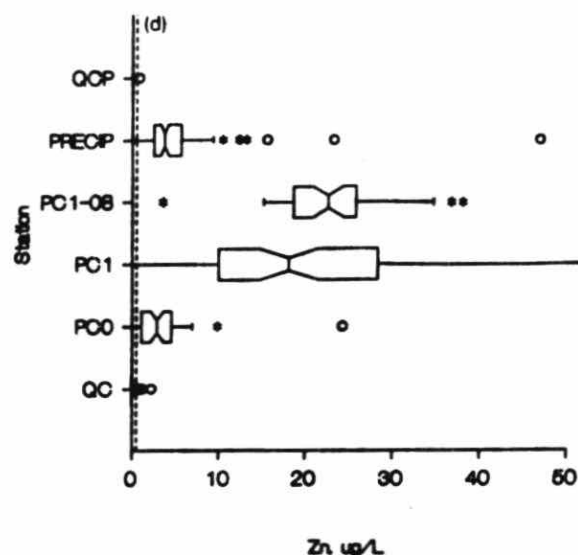
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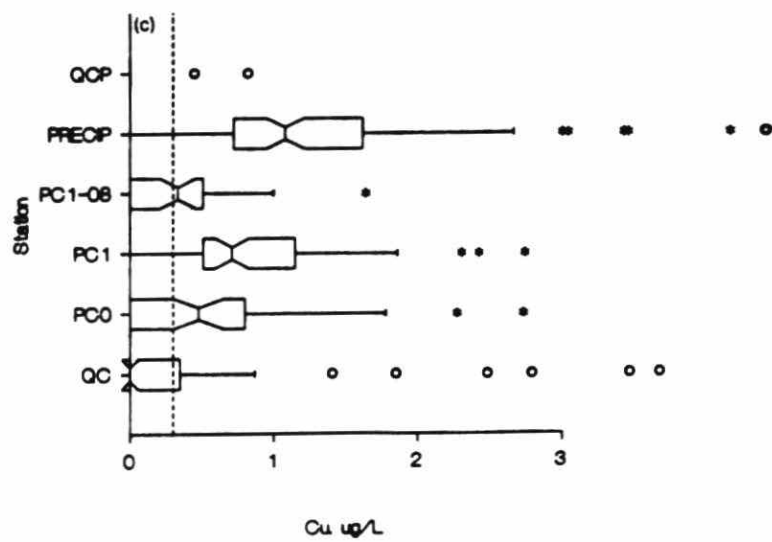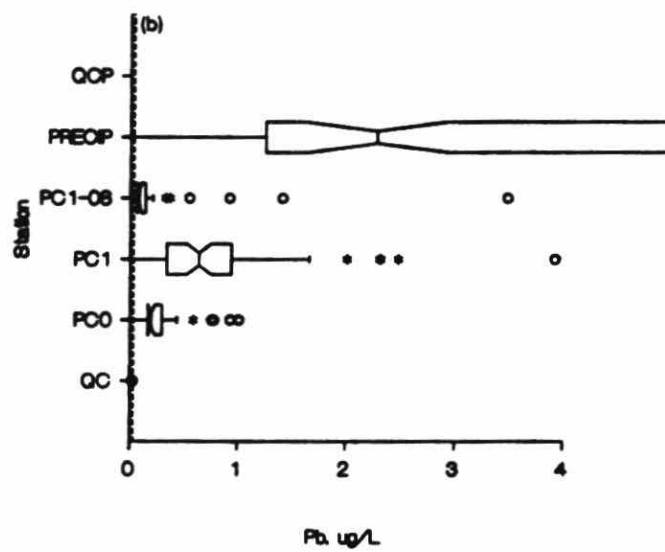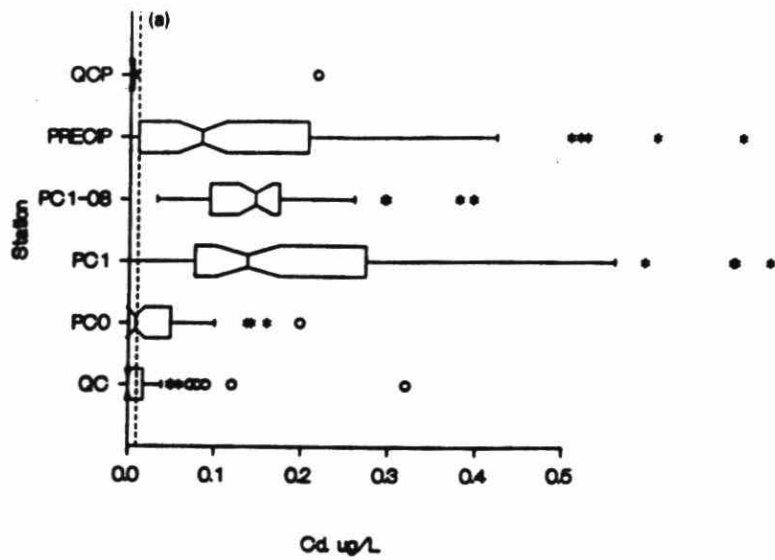
Fig. 3. Notched box plots of Cd, Pb, Cu and Zn from the three surface water sites and the surface water field quality control samples (QC). Total precipitation and QCP is also provided for comparison.

DISCUSSION

The median concentrations of trace metals in precipitation reported here are reasonably close to the annual volume-weighted geometric mean values reported by the Air Resources Branch of the Ontario Ministry of the Environment for their monthly cumulative wet-only collector at Dorset Ontario (OME, 1984–1986); they reported 0.03–0.07, 2.83–4.70, 0.4–1.1 and 3.5–5.2 $\mu g \, l^{-1}$ for Cd, Pb, Cu and Zn, respectively, versus the 0.08, 2.28, 1.1 and 3.7 $\mu g \, l^{-1}$ reported
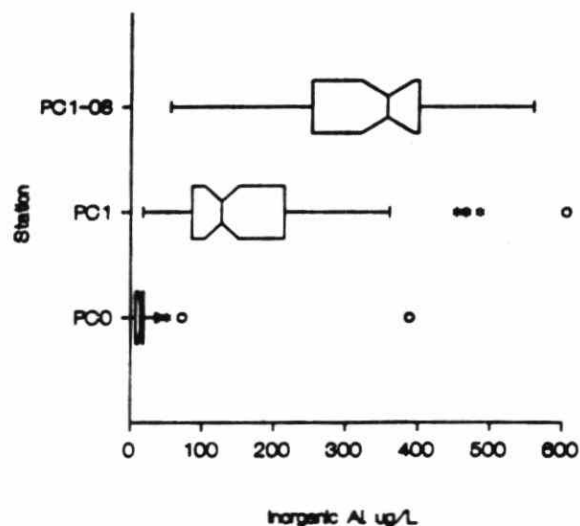

Fig. 4. Notched box plot of inorganic Al from the three surface water sites, derived from LaZerte (1989).

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here. The values reported here are more useful for comparative purposes, because they are more recent, they represent three wet-only collectors, and they cover exactly the same time frame as do the surface water samples.

Cadmium and Zn appear to be exported from these upland soils, perhaps from the mineral horizons. Their behaviour follows that of inorganic Al, which is known to be exported from the mineral (B) soil horizons (Fig. 4, from LaZerte, 1989). All eight stations in a less acidified catchment (LaZerte, unpublished results) have median zinc concentrations substantially less than those reported here for PC1-08 and PC1; also, only one of these stations has Cd levels as high as PC1-08 and PC1, but this station also has a lower pH and the highest inorganic Al relative to the others. In general, this confirms other reports (Tyler, 1978; Biddapa et al., 1982; Bergkvist, 1987) and reviews (Campbell et al., 1985; LaZerte, 1986) suggesting increased export of Cd and Zn from soils impacted by acidic deposition.

Conversely, Pb and Cu are not exported from the upland soils. Their behaviour follows closely that of dissolved organic carbon (DOC) and organic Al (Fig. 5, from LaZerte, 1989). Presumably, the high levels of Pb and Cu in precipitation are tightly bound in the organic surface layer of the soils (Tyler, 1978; Biddapa et al., 1982; Johnson et al., 1982; Freidland et al., 1984; Bergkvist, 1987). Although theoretically these metals might be transported out of the soil bound to water-soluble organics, in fact these soils do not export appreciable amounts of organics (LaZerte and Dillon, 1984). Dissolved organic carbon exported in the organic form only as far as the mineral (B) soil horizons (Tyler, horizons of the soil (LaZerte, 1989). We expect then that Pb and Cu deposited on these soils behave just like organic Al (LaZerte, 1989); i.e., they are partially exported in the organic form only as far as the mineral (B) soil horizons (Tyler, 1981; Bergkvist, 1987).

Although their median values are lower, there is no significant difference between the Cd and Zn levels at PC1 and PC1-08. However, the wetlands do add substantial real variability, which is the result of distinct seasonal changes in wetland chemistry (LaZerte and Dillon, 1985). In addition, it may be that some part of the acid-labile Cd and Zn becomes organically bound within the wetland as happens with Al (LaZerte, 1989).

Increased seasonal variability in the concentrations of Pb and Cu from PC1 is also found. More important, however, is the large increase in their concentrations at PC1. Given the lower inputs from the upland soils, direct deposition onto the wetland surface may be a major source, followed by complexation with fulvic acids and transport to the lake. Although detailed flux estimates are not available at this time, it may be that wetland export of Pb and Cu constitutes a significant fraction of Plastic Lake's inputs (Borg and Johansson, 1988; however, see Evans et al., 1986). These correlations with DOC transport and the suggested behaviour in the upland soils is consistent with what is known about the relatively high affinities of fulvic acids and other organics for Pb and Cu; Cd and Zn, on the other hand, have lower affinities (Campbell et al., 1985).
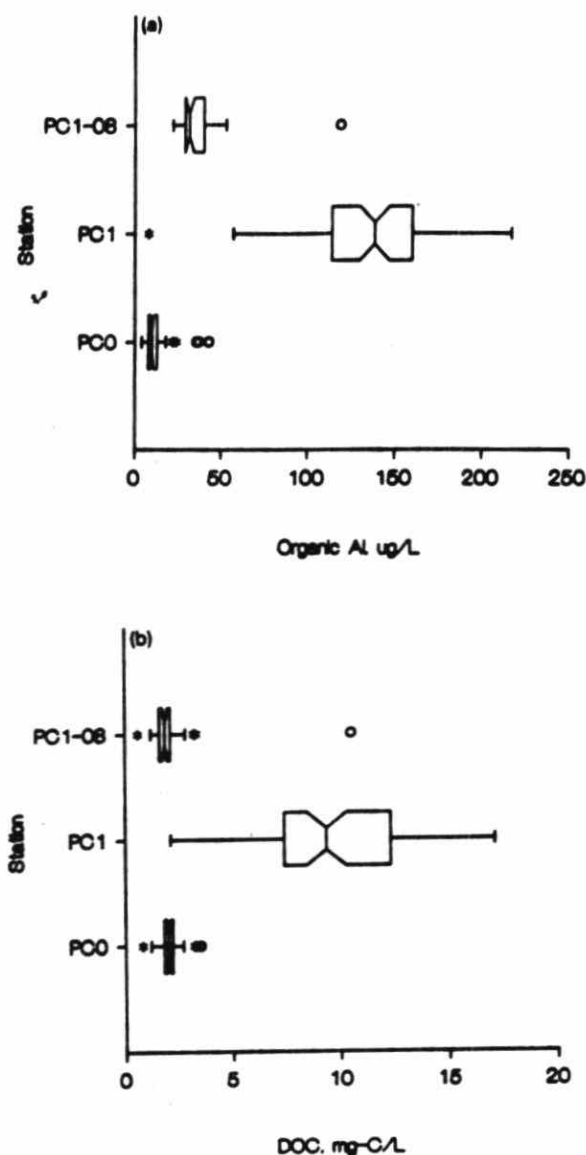
Fig. 5. Notched box of organic Al and DOC from the three surface water sites, derived from LaZerte (1989).

Our results show a substantial decrease in all four trace metals in Plastic Lake as measured at the outflow (PC0). Nonetheless, catchment acidification has probably increased the loading of Cd and Zn (as well as Al and Mn) from the upland soils much more than lake acidification has reduced their retention within the lake (LaZerte, 1986; Dillon et al., 1987). Elevated Cd levels in Plastic Lake relative to lakes with a more neutral pH (Stephenson and Mackie, 1988) also suggest this.

Given the evidence that Pb and Cu closely follow the transport of organics in water, and knowing that lake acidification has decreased the concentration of DOC in Plastic Lake (Dillon et al., 1987), we could propose that Pb and Cu

concentrations in the lake also decrease with acidification. However, the magnitude of this effect would depend upon the proportion of the metal transported to the lake from the surrounding wetlands relative to direct deposition on the lake surface, and on the relative impact of lake acidification on the retention of metal from these different sources. For example, Dillon et al. (1986, 1988) have reported lowered Pb retentions in exceptionally acid lakes in the Sudbury smelting area, and Borg (1983) reports an increase in Pb concentrations in regionally acidified lakes of Sweden, independent of metal deposition gradients. These reports imply that lake acidification decreases the retention of the more abundant atmospherically deposited inorganic Pb more than it increases the retention of the less abundant organic Pb from terrestrial sources.

ACKNOWLEDGEMENTS

REFERENCES

Bergkvist, B., 1987. Soil solution chemistry and metal budgets of spruce forest ecosystems in S. Sweden. Water, Air Soil Pollut., 33: 131–154.

Biddapa, C.C., M. Chino and K. Kumazawa, 1982. Migration of heavy metals in two Japanese soils. Plant Soil, 66: 299–316.

Borg, H., 1983. Trace metals in Swedish natural fresh waters. Hydrobiologia, 101: 13–18.

Borg, H. and K. Johansson, 1988. Metal fluxes to Swedish forest lakes. In: H. Borg (Ed.), Trace Metals in Swedish Forest Lakes — Factors Influencing the Distribution and Speciation in Water. Ph.D. thesis, Uppsala University, Sweden.

Campbell, P.G., P.M. Stokes and J.N. Galloway, 1985. Acid Deposition: Effects on Geochemical Cycling and Biological Availability of Trace Elements. Subgroup on Metals of the Tri-academy Committee on Acid Deposition. National Academy Press, Washington, DC, 83 pp.

Chambers, J.M., W.S. Cleveland, B. Kleiner and P.A. Tukey, 1983. Graphical Methods for Data Analysis. Duxbury Press, Boston, 395 pp.

Dillon, P.J., P.J. Scholer and H.E. Evans, 1986. ^{210}Pb fluxes in acidified lakes. In: P.G. Sly (Ed.), Sediments and Water Interactions. Springer-Verlag, New York, pp. 491–497.

Dillon, P.J., R.A. Reid and E. de Grosbois, 1987. The rate of acidification of aquatic ecosystems in Ontario, Canada. Nature, 329: 45–48.

Dillon, P.J., H.E. Evans and P.J. Scholer, 1988. The effects of acidification on metal budgets of lakes and catchments. Biogeochemistry, 5: 201–220.

Evans, H.E., P.J. Dillon, P.J. Scholer and R.D. Evans, 1986. The use of Pb/^{210}Pb ratios in lake sediments for estimating atmospheric fallout of stable lead in South-Central Ontario, Canada. Sci. Total Environ., 54: 77–93.

France, R.L. and B.D. LaZerte, 1987. Empirical hypothesis to explain the restricted distribution of *Hyallela azteca* (Amphipoda) in anthropogenically acidified lakes. Can. J. Fish. Aquat. Sci., 44: 1112–1121.

Freidland, A.J., A.H. Johnson and T.G. Siccama, 1984. Trace metal content of the forest floor in the Green Mountains of Vermont: spatial and temporal patterns. Water, Air Soil Pollut., 21: 161–170.

Johnson, A.H., T.G. Siccama and A.J. Friedland, 1982. Spatial and temporal patterns of lead accumulation in the forest floor in the Northeastern United States. J. Environ. Qual., 11: 577–580.

LaZerte, B.D., 1984. Forms of aqueous aluminum in acidified catchments of Central Ontario: a methodological analysis. Can. J. Fish. Aquat. Sci., 41: 766–776.

LaZerte, B.D., 1986. Metals and acidification: an overview. Water, Air Soil Pollut., 31: 569–576.

LaZerte, B.D., 1989. Aluminum speciation and organic carbon in waters of Central Ontario. In: T.E. Lewis (Ed.), Environmental Chemistry and Toxicology of Aluminum. A.C.S. Symposium, New Orleans, LA. Lewis, Chelsea, MI, pp. 195–207.

LaZerte, B.D. and P.J. Dillon, 1984. Relative importance of anthropogenic versus natural sources of acidity in lakes and streams of Central Ontario. Can. J. Fish. Aquat. Sci., 41: 1664–1677.

LaZerte, B.D. and P.J. Dillon, 1985. Chemical transformations of stream and soil water flowing through *Sphagnum*-conifer swamps of Central Ontario. Abstr. Int. Symp. Acidic Precipitation, Muskoka, Ont., Canada.

OME, 1984–1986. Annual Statistics of Concentration and Deposition — Cumulative Precipitation Monitoring Network. Ontario Ministry of the Environment, Acidic Precipitation in Ontario Study, Dorset, Ont.

Stephenson, M. and J.L. Mackie, 1988. Total cadmium concentrations in the water and littoral sediments of Central Ontario lakes. Water, Air Soil Pollut., 38: 121–136.

Tyler, G., 1978. Leaching rates of heavy metal ions in forest soil. Water, Air Soil Pollut., 9: 137–148.

Tyler, G., 1981. Leaching of metals from the A-horizon of a spruce forest soil. Water, Air Soil Pollut., 15: 353–369.